Suomen ympäristökeskuksen moniste

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Irma Mäkinen and Pirjo Sainio

SYKE Proficiency test 8/2004

Mineral oil hydrocarbons in water

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FINNISH ENVIRONMENT INSTITUTE

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CONTENT

ANNECES

1. INTRODUCTION

The Finnish Environment Institute carried out the proficiency test for the determination of mineral oil hydrocarbons in water by using GC methods in February 2005.

The proficiency test was carried out in accordance with the international guidelines, ISO/IEC Guide 43 1 (1), ILAC Requirements (2), ISO/DIS 13528 (3) and the Draft IUPAC/AOAC recommendations for proficiency testing (4).

The former SYKE interlaboratory comparison for analysis of mineral oil in water was carried out in 2002.

2. ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

The responsibilities in organizing the proficiency test were as follows:
Irma Mäkinen, SYKE, coordinator
Pirjo Sainio, SYKE, analytical expert

2.2 Participants

A total of 18 laboratories from Finland and Sweden participated in the proficiency test (Annex 1). One laboratory (lab 18) has not received the information letter. They received and analyzed the samples in April 2005.

2.3 Sample preparation and delivery

The synthetic sample S1 was prepared from the mixture of diesel and lubricating oil (see Table 1). The separately prepared solutions of known concentration of diesel and lubricating oil were mixed to prepare the addition solutions V1 and V2. The sample preparation is presented in Annex 2. Before delivery, the sample ampoules were weighed to check the possible solvent evaporation.

Two water samples, one litre of each, were delivered. The sample V1 was a lake water (the Lake Päijänne) and the sample V2 was a river water (the river Mustionjoki). Laboratories were asked to add the precise amount of respective addition solution (V1: 100 µl, V2: 200 µl) into the samples.

The proficiency test took place between 9th February and 11th February 2005.

The results as well as chromatogrammes were asked to return by 22nd February 2005.

Table 1. Samples of the proficiency test 8/2004

Samples	Sample type
L1: the mixture of diesel/fuel and lubricating oil (1:1)	1 synthetic solution in hexane
V1: the lake water	1 lake water + addition of the mixture of diesel/fuel and lubricating oil (2:3)
V2: the river water	1 river water + addition of the mixture of diesel/fuel and lubricating oil (3:5)

2.4 Sample testing

2.4.1 Homogeneity study

Sample preparation of the synthetic solutions was tested by analysing the mineral oil mixtures in the ampoules S1, V1 and V2 (Annex 3). In the synthetic sample S1 the recovery of the mineral oil content was between 95 % and 105 %. In the solutions prepared for the water samples (V1 and V2) the obtained results were between 95 % and 105 % of the mean value.

2.4.2 Stability study

Stability testing of the samples was based on the analyses carried out at three times: once before the delivery and twice during the proficiency test. There was not found a change higher than 105 % or less than 95 % in the content of mineral oil during the testing period (Annex 3).

2.5 Comments sent by the participants

The participants commented on their results or samples or analytical methods (Annex 4).

2.6 Analytical methods

The standard method EN ISO 9377-2 has been published for analysis of mineral oil in water (5). In the proficiency test hexane was mainly used as an extraction solvent and the used volume varied between 10 and 50 ml. The samples were extracted either by shaking or stirring. The extraction time varied between 20 and 60 minutes.

The mineral oil content between n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$) was measured by GC-method (Annex 5.1). The participants have mainly used their own mixtures of mineral oil for calibration. Only six participants used the commercial mixture from BAM. Florisil/Na_2SO_4 column used on the clean-up step was mainly prepared at the participating laboratory. Some laboratories used Al_2O_3 instead of Florisil.

One laboratory (lab 15) used the gravimetric method for the measurement of mineral oil after extraction.

2.7 Data treatment

2.7.1 Testing of outliers and normality of data

Before the statistical treatment, the data was tested according to Kolmogorov-Smirnov normality test. Outliers were rejected according to the Hampel test before calculation of the mean value (Annex 6). One result (lab 7) was rejected manually in robust statistics as an outlier in analysis of the sample V1, because it deviated more than 100 % from the robust mean.

2.7.2 Assigned value and its uncertainty

For the synthetic sample S1 the calculated mineral oil content was used as the assigned value. For the analysis of the water samples V1 and V2 the robust mean value calculated according to the robust algorithm A was used as the assigned value (Annex 6). The assigned values have not been changed, after the Laboratory 18 reported their results in April 2005. The originally calculated robust means have been used as the assigned values.

The uncertainty of the assigned value was calculated using the standard deviation based on the robust standard deviation. The uncertainties were between 2,8% and 5,5% (Annex 7).

2.7.3 Target value for total standard deviation

The target total standard deviation (s_{target}, %) used for calculation of the z scores was estimated on basis of the mineral oil content of the samples, the variation of the results and the measurement uncertainties reported by the participants. The s_{target} was 20 % (95 % confidence interval) for the analysis of the solvent sample S1. For the analysis of the water samples V1 and V2 the s_{target} was 35 % and 30 %, respectively.

2.7.4 Evaluation of performance

The performance evaluation was carried out by using the z scores. The z scores were calculated using the following equation:

$$z = (x_i - X)/s$$

where
x_i = the reported value of the participant
X = the assigned value
s = the target total standard deviation (s_{target}).

z scores can be interpreted as follows:

$\lvert z \rvert < 2$	"satisfactory" results
$2 \leq \lvert z \rvert \leq 3$	"questionable" results
$\lvert z \rvert > 3$	"unsatisfactory" results.

The z scores are presented in Annex 8 and the summary of z scores is presented in Annex 9.

The organizing laboratory (SYKE) had the code 17 in this proficiency test.

3. RESULTS AND PERFORMANCE OF THE PARTICIPANTS

3.1 Results

The results of the standard solution (the sample S1) showed a good agreement between the the participants (SD = 12 %) comparing with the results obtained in the former proficiency test in 4/2002 (6), when the respective standard deviation was 21 %. This is mainly due to experience in use of the standard method (EN ISO 9377).

Table 2. Summary of the proficiency test 8/2004

Analyte	Sample	Unit	Ass. val.	Mean	Md	SD	SD%	2*Targ SD%	Num of labs	Ac-cepted. z-val%
Min.oil-GC	S1	mg/ml	12	12,22	12,07	1,625	13,3	20	16	88
	V1	mg/l	1,02	1,018	1,035	0,2242	22	35	17	82
	V2	mg/l	6,38	6,393	6,71	1,157	18,1	30	17	94

where,

Ass. val.	Assigned value
Mean	Mean value
Mean rob	Robust standard deviation
SD rob	Robust standard deviation
SD rob %	Robust standard deviation as percents
2*Targ. SD%	Target total standard deviation (95 % confidence interval) in evaluation of performance
Num of Labs	Number of participants
Accepted z-val%	Satisfied z values: the results (%), where $\lvert z \rvert \leq 2$.

In the analysis of the water samples, V1 and V2, the standard deviations were 22 % and 19 %. They were about 10%-15% lower than in the former proficiency test 4/2002 (6).

In this proficiency test two laboratories reported that their method is under construction. The extraction was mainly done by shaking (Annex 5.1).The results obtained by using shaking in extraction were mainly higher than the results obtained by stirring (Annex 5.2). In analysis of mineral oil hydrocarbons extraction and cleanup are the most crucial steps (7). Extraction time and magnetic stirring speed are the crucial parameters particularly for the analysis of water samples (7). Some participants reported about emulsions in extraction (Annex 5.1). Emulsions are avoided by laminar stirring (7). In this proficiency test the participants used mainly Florisil column prepared by themselves. Variances in water content of Florisil can affect its activity. Recoveries of hydrocarbons can decrease, if Florisil is highly activated. Also, the added mineral oil might be adsorbed on the walls of a sample vessel.

The small amount of C41 solution was added to the waters V1 and V2 for the verification that extraction was really made with those waters. Eleven laboratories of all were sent the chromatogrammes as was asked to. In the chromatogrammes of six laboratories the signal of C41 was clearly visible. An example of sample chromatogram is presented in Annex 11.

The reported measurement uncertainties in analysis of each sample varied rather much (10% - 40 %) between different participants (Annex 12).

3.2 Estimation of performance

In this proficiency test 88 % of the participating laboratories reported satisfactory results, based on the target total standard deviation 20% - 35% used in calculating of z scores in 95 % confidence interval (Annex 9). Six participants used the accredited analytical methods and 100% from their results were satisfactory.

The water samples V1 and V2 turned to be the most crucial to analyse. Some improvements in analytical techniques (e.g. extraction efficiency, clean-up) might increase the reliability of the results in future.

The Finnish proficiency test for analysis of mineral oil hydrocarbons in waters by using the GC method was carried out for the second time. These results have improved since the last comparison in 2002.

4. SUMMARY

The Finnish Environment Institute carried out the profiency test for analysis of mineral oil hydrocarbons in waters by using GC methods in February 2005. A total of 18 laboratories from Finland and Sweden participated.

One standard solution containing a known concentration of different oils was prepared. Two solutions containing different oils were prepared to be used as the addition solutions for the preparation of water samples. One river water sample and one lake water sample were delivered.

For the synthetic sample the calculated mineral oil content was used as the assigned value. For the analysis of the water samples the robust mean value was used as the assigned value.

In this proficiency test, 88 % of the participating laboratories reported acceptable results, based on the target total standard deviation 20 % – 35 % used in calculating of z scores in 95 % confidence interval. Six participants used the accredited analytical methods and 100% from their results were satisfactory.

The Finnish proficiency test for analysis of mineral oil hydrocarbons in waters by using the GC method was carried out for the second time. These results have improved since the last comparison in 2002.

5. YHTEENVETO

Suomen ympäristökeskus järjesti helmikuussa 2005 pätevyyskokeen mineraaliöljyn määrittämiseksi vedestä. Pätevyyskokeessa käytettiin yhtä poikkeusta lukuun ottamatta kaasukromatografisia määritysmenetelmiä. Pätevyyskokeeseen osallistui kaikkiaan 18 laboratoriota Suomesta ja Ruotsista.

Pätevyyskokeen näytteinä oli yksi tunnetun öljypitoisuuden omaava standardiliuos ja kaksi vesinäytettä, joihin osallistuva laboratorio teki toimitetut mineraaliöljylisäykset.

Synteettiselle näytteelle käytettiin vertailuarvona laskennallista öljypitoisuutta. Vesinäytteille vertailuarvona käytettiin robusti-keskiarvoa.

Tässä pätevyyskokeessa osallistujien tuloksista 88% oli tyydyttäviä, kun z-arvojen laskennassa käytettiin 20% – 35 %:n tavoitekokonaiskeskihajontoja. Vesinäytteiden analysoinnissa esiintyi joitakin eroja analyysimenetelmän eri vaiheissa (mm. uutto, puhdistus), joilla on ollut vaikutusta tuloksiin.

Määritysmenetelmänsä akkreditoineiden laboratorioiden tuloksista 100% oli tyydyttäviä.

Pätevyyskoe mineraaliöljyn määrittämiseksi vesistä GC-menetelmää käyttäville laboratorioille järjestettiin toisen kerran Suomessa. Tulokset olivat parantuneet edellisestä pätevyyskokeesta, joka järjestettiin vuonna 2002.

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ANNEX 1. PARTICIPANTS IN THE INTERLABORATORY COMPARISON 8/2004

Alcontrol Laboratories AB, Linköping, Sweden

AnalyCen laboratoriot, Tampere, Finland

Borealis Polymers Oy, laboratoriopalvelut, Porvoo, Finland

Ekokem Oy Ab, Riihimäki, Finland

Fortum Oil Oy, kehittäminen ja kenttälaboratoriot, Porvoo, Finland

Fortum Oil Oy, Porvoon jalostamon laboratorio, Porvoo, Finland

Helsingin kaupungin ympäristökeskus, ympäristölaboratorio, Helsinki, Finland

Insinööritoimisto Paavo Ristola Oy, Hollola, Finland

Karlshamn Kraft AB, Karlshamn, Sweden

Lahden Tiede- ja yrityspuisto, Oy, Lahden tutkimuslaboratorio, Lahti, Finland

Nab Labs Ympäristöanalytiikka Oy, Oulu, Finland

Nab Labs Ympäristöanalytiikka Oy/Juve Ac, Rovaniemi, Finland

Novalab Oy, Karkkila, Finland

Raisio Yhtymä, ympäristö- ja alkuainelaboratorio, Raisio, Finland

SGS Inspection Services Oy, Hamina, Finland

Suunnittelukeskus Oy, Helsinki, Finland

SYKE, Laboratory, Finland

Vattenlaboratoriet VA-Verket, Malmö, Sweden

ANNEX 2. PREPARATION OF THE SAMPLES

The standard solution L1

Oil type	Preparation of stock solutions	Preparation of sample L1
I: Diesel/Fuel oil (BAM KS 5004)	2000 mg oil in 50 ml of hexane => 40 mg/ml	30 ml I + 70 ml of hexane => **11,6 mg/ml**

The prepared solution was carefully mixed and sampled into a 2 ml portions. Small amber glass bottles with a teflon-lined screw cap were used. Bottles were labelled and numbered according to filling order. The weight of each bottle was recorded.

The addition solutions V1 and V2

Oil type	Preparation of stock solutions	Preparation of sample V1	Preparation of sample V2
I: Diesel/Fuel oil (BAM KS 5002)	3000 mg oil in 50 ml of isopropanol => 59 mg/ml	10 ml I + 10 ml II into 100 ml of isopropanol => **11,76 mg/ml**	20 ml I + 40 ml II into 100 ml of isopropanol => **35,27 mg/ml**
II: Lubricating oil (BAM KS 5003)	3000 mg oil in 50 ml of isopropanol => 59 mg/ml		
The resulting water sample concentration		100 µl into 1 litre of water => **1,18 mg/l**	200 µl into 1 litre of water => **7,05 mg/l**

The prepared solutions were carefully mixed and sampled into a 2 ml portions. Small glass bottles with a teflon-lined a screw cap were used. Bottles were labelled and numbered according to filling order. The weight of each bottle was recorded.

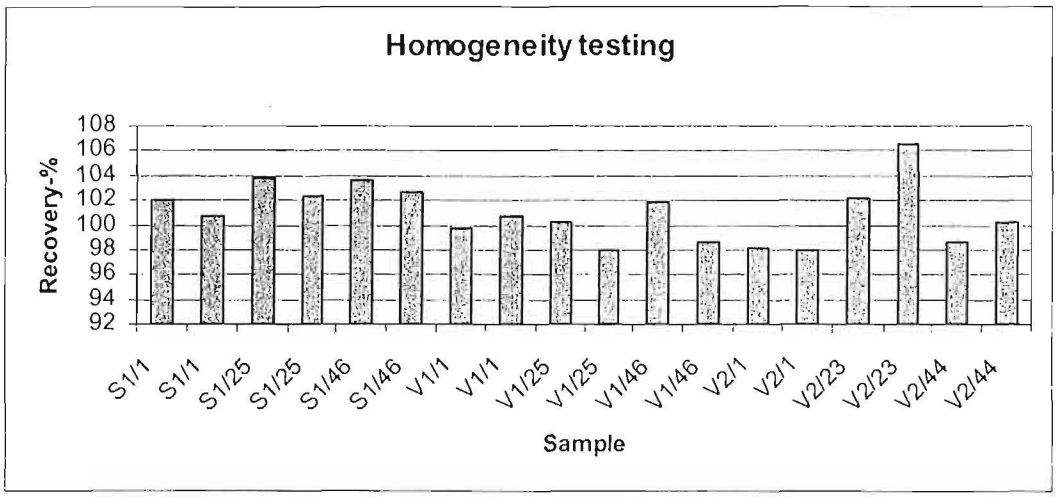
Solution of C41 was added into the waters V1 and V2.

ANNEX 3. RESULTS OF THE HOMOGENEITY AND STABILITY STUDIES

The solvent sample L1 and the solutions for the water samples V1 and V2

Homogeneity

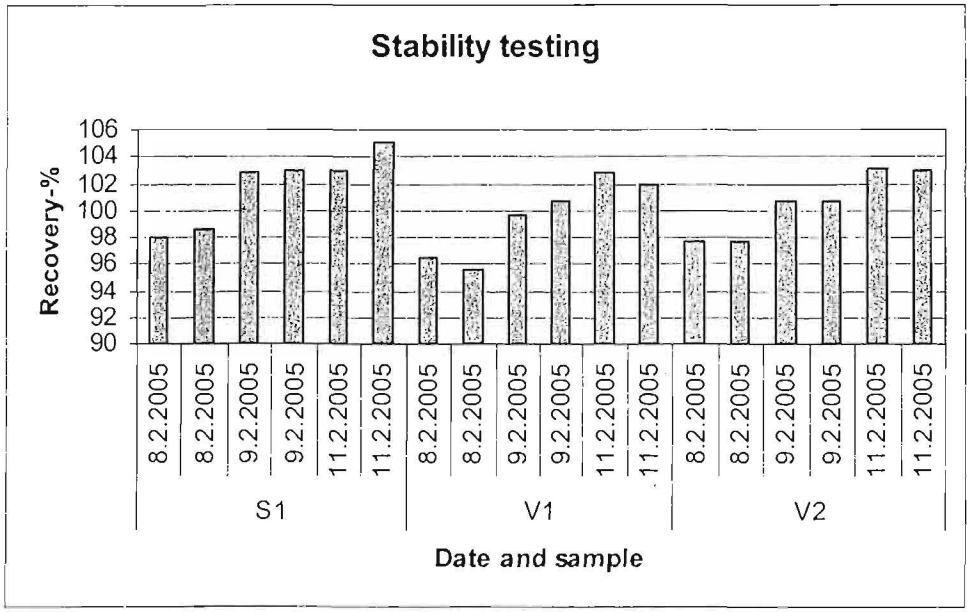
Preparation and distribution of the synthetic solutions L1 (the synthetic sample), V1 and V2 (the addition solution for the water samples) was tested by analysing three ampoules as duplicates.



The obtained mineral oil content was between 102 % and 104 % of the calculated mineral oil content in the tested subsamples in the solvent sample L1 or 98 % and 107 % of the mean value mineral oil content in the solutions prepared for the water samples V1 and V2. In the sample ampoule V2/23 the mean value of the duplicates was 104,4 % (< 105 %).

Stability

Stability study was based on the analyses carried out three times after delivery of the samples.



The mineral oil content in the ampoules was between 96 % and 105 % from the calculated mineral oil content in 8th - 11th February, 2005. In the sample ampoule S1/11.2.2005 the mean value of the duplicates was 104,1 % (< 105 %).

ANNEX 4. COMMENTS SENT BY THE PARTICIPANTS

Lab	Comment	Action/SYKE
5	The volume of the water samples was missing for calculation of the results. It was 1 litre.	The volume has been informed.
8	The laboratory reported the incorrect LD.	The LD was corrected in the list of analytical methods.
18	The laboratory did not received the information letter. The samples had been distributed 5th April 2005 and the samples were analyzed 6th April 2005.	The results were included in the data file.
2	The volume in the S1 ampoule was only about 2 ml – not 3 ml? The sample V2 contained also hydrocarbons with higher boiling point than C40 – not included in the calculation of oil index.	The prepared amount of solutions was fixed to be 2 ml in order to minimize the number of extra bottles.
11	Extraction solvent did not included n-decane and n-tetracontane	—
15	Gravimetric determination	—

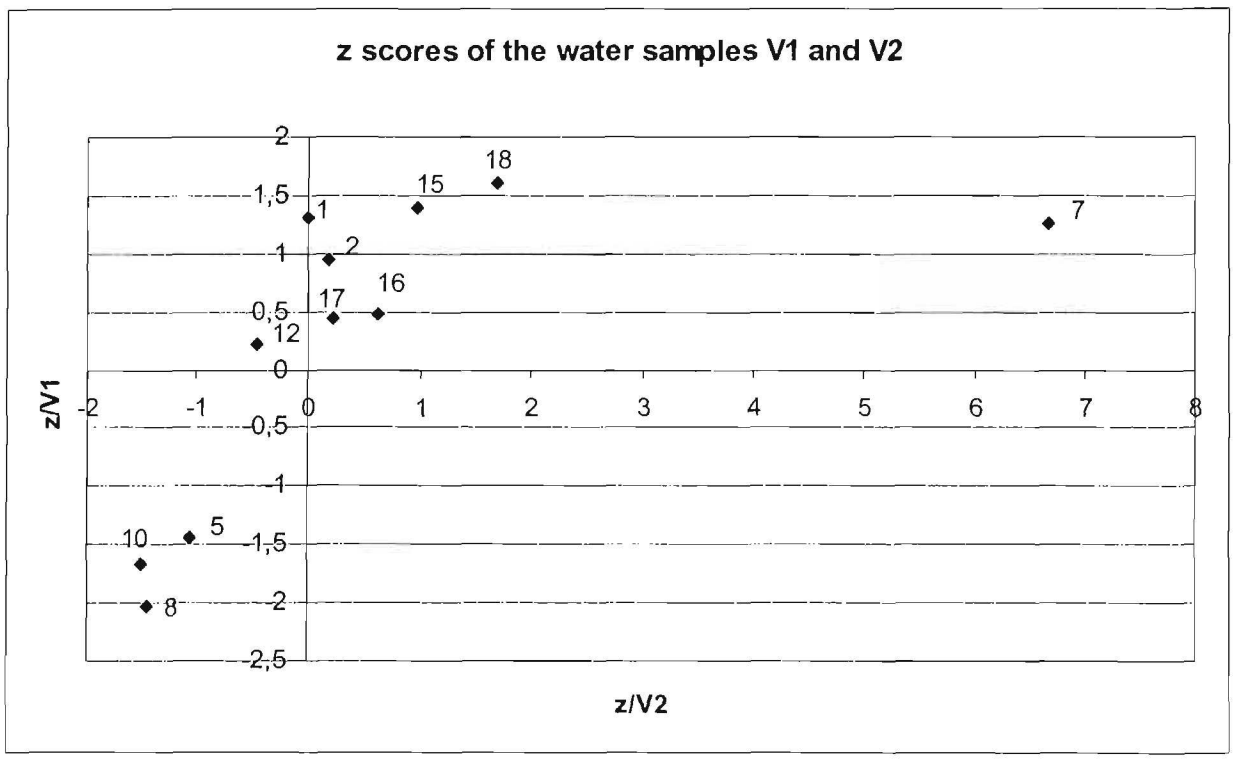
ANNEX 5.1 ANALYTICAL METHODS

Lab	Acidification	Extraction solvent	Extraction method	Separa-tion	Emulsion	Drying	Florisil	Injection	GC-column	m/mm/µm	FID T°C	Gas mL/min	Standard	Range; DL (mg/l)
1	HCl	hexane,50 ml	shaking, 30	funnel	centrif.	Na_2SO_4	ready	autom., 1 µl	3WDB-5MS	30/0,35/0,25	325	He, 5,9	BAM	0,1-20; 0,1
2	pH 2/$MgSO_4$	hexane,50 ml	shaking, 30	funnel	no probl.	Na_2SO_4	itself	LVI+split, 20 µl	CP-Sil %CB	25/0,53/1	325	N_2, 20	own	0,1-5; 0,1
4	HCl	hexane,50 ml	shaking, 60	funnel	centrif.	No	itself	PTV, 2 µl	DB5-MS	28,8/0,25/0,25	MS-det.	He, 1,3	BAM	0,05-2
5		hexane,10 ml	stirring, 60	manual	exc.hex.	Na_2SO_4	Al_2O_3	splitless, 2 µl	DB-1	15/0,53/0,15	340	He	own	0,3-8; 0,1
6	pH 2/$MgSO_4$	pentane,25 ml	_, 30	funnel	centrif.	Na_2SO_4			DB-5				own	
7	pH 2	pentane,50 ml	shaking, 30	funnel	some probl.	Na_2SO_4	ready	PTV, 40µl	CP-SIL 8CB-MS	30/0,25/0,25	400	He 5,6	own	0-10; 0,02
8	HCl	hexane,50 ml	stirring, 50	funnel	no probl.	Na_2SO_4	itself	splitless, 1 µl	HP-5MS	27/0,25/250	MS-det.	He 1,0	BAM	0,005-1; 0,2
9	HCl	hexane,50 ml		funnel		Na_2SO_4	itself	splitless, 1 µl	CP-SIL 5CB	15/0,32/0,25	325	He 1,0	own	0-2; 0, 035
10	pH 2/$MgSO_4$	hexane,50 ml	shaking, 20	funnel	no probl.	Na_2SO_4	itself	splitless, 2 µl	NB-1	15/0,32/0,1	320	He 1,5	BAM	0,1-1; 0,1
11		hexane,35 ml		funnel	no probl.		Al_2O_3	autom., 2 µl	DB-5	30/0,32/0,25	350	He 2,1	BAM	0,05-20; 0,05
12	HCl	hexane,50 ml	shaking, 30	micro-sep.	some probl.	No	itself	on-colum., 5 µl	CP-SIMDIST	5/0,53/0,88	430	He 20	own	0,1-1,2; 0,1
13		hexane	Soxlet						Gravimetric					
15	NaCl	hexane,50 ml	shaking, 30	funnel	no probl.	Na_2SO_4	itself	on-colum., 0,5 µl	HP 5	30/0,32/0,25	300	He 1,5	own	0,1-60; 0,1
16	pH 2	hexane,50 ml	shaking, 30	funnel		Na_2SO_4	itself	on-colum., 2 µl	SGP BPX5	18,3/0,32/1	360	He 3,4	own	0,2-1,2; 0,03
	pH 2/$MgSO_4$								S/M 3041C15					
17	HCl	hexane,30 ml	stirring, 30		no probl.	No	itself	on-colum., 1 µl	SGE DPX-5	5/0,32/1	340	He 2	BAM	0,1-7,9; 0,1
18	HCl	heptane+ n-tetracontane + decane	stirring, 40			Na_2SO_4	Al_2O_3	split-autom., 2 µl	Agilent 19091	12/0,32/0,25	300			0,1-2

ANNEX 5.2 RESULTS OBTAINED BY DIFFERENT ANALYTICAL METHODS (the water samples V1 and V2)

Extraction procedure:

Lab	
1	shaking 30 min, hexane 50 ml
2	shaking 30 min, hexane 50 ml
4	shaking 30 min, hexane 5 ml
5	stirring 60 min, hexane 10 ml
7	shaking 30 min, pentane 50 ml
8	stirring 50 min, hexane 50 ml
10	shaking 20 min, hexane 50 ml ml
12	shaking 30 min, hexane 50 ml
13	Soxlet, hexane
15	shaking 30 min, hexane 50 ml
16	shaking 30 min, hexane 50 ml
17	stirring 30 min, hexane 30 ml
18	stirring 40 min, heptane + decane + n-tetracontane



ANNEX 6. EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant (Annex 8):

Analyte	Min.oil-GC
Unit	mg/kg or mg/ml
Sample	The code of the sample
z-Graphics	z score - the graphical presentation
z-value	z-score, calculated as follows: $z = (x_i - X)/s$, where x_i = the result of the invidual laboratory X = the reference value (the assigned value) s = the target value for the total standard deviation (s_{target}).
Outl test OK	yes - the result passed the outlier test), H = Hampel test (a test of mean values)
Assigned value	the reference value
2* Targ SD %	the target total standard deviation (95 % confidence interval).
Lab's result	the result reported by the participant (the mean value of the replicates)
Md.	Median
Mean	Mean
Mean rob	Robust men
SD rob	Robust standard deviation
SD rob %	Robust standard deviation, %
SD	Standard deviation
SD%	Standard deviation, %
Passed	The results passed the outlier test
Missing	i.e. < DL
Num of labs	the total number of the participants

Summary on the z scores (Annex 7):

A - accepted ($-2 < z \leq 2$)
p - questionable ($2 < z \leq 3$), positive error, the result > X
n - questionable ($-3 \leq z < -2$), negative error, the result < X
P- non- accepted ($z > 3$), positive error, the result >>> X
N- non- accepted ($z < -3$), negative error, the result <<< X (X = the reference value)

Robust analysis (Calculation of the assigned value for the samples V1 and V2)

The items of data is sorted into increasing order, $x_1, x_2, \ldots, x_i, \ldots, x_p$.

Initial values for X^* and s^* are calculated as:

X^* = median of x_i (i = 1 ...p)
$s^* = 1.483$ median of $| x_i - x^* |$ (i = 1 ...p)

The values of X^* and s^* are updated by calculating
$\varphi = 1.5\ s^*$

For each x_i is calculated:

$x_i^* = x^* - \varphi$ if $x_i < x^* - \varphi$
$x_i^* = x^* + \varphi$ if $x_i > x^* + \varphi$
$x_i^* = x_i$ otherwise

The new values of x^* and s^* are calculated from:

$$X^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergenes.

Ref: Statistical methods for use in proficiency testing by interlaboratory comparisons, Annex C (ISO/DIS 13528, Draft 2002-02-18)

ANNEX 7. THE ASSIGNED VALUES AND THEIR UNCERTAINTIES

Assigned values

Sample	Assigned value	Estimation of assigned value	Uncertainty (U = 2 u_c), %
S1	12 mg/ml	Calculated concentration	2,8
V1	1,02 mg/l	Robust mean	5,5
V2	6,38 mg/l	Robust mean	4,7

$u_c = s^*/\sqrt{p}$

where
s^* = the robust-standard deviation
p = the number of the results

ANNEX 8. RESULTS OF EACH PARTICIPANT

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
Min.oil-GC	mg/ml	S1		0,500	yes	12	20	12,60	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		0,000	yes	1,02	35	1,02	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		1,296	yes	6,38	30	7,62	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 2																
Min.oil-GC	mg/ml	S1		0,750	yes	12	20	12,90	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		0,168	yes	1,02	35	1,05	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		0,951	yes	6,38	30	7,29	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 3																
Min.oil-GC	mg/ml	S1		-1,168	yes	12	20	10,598	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		-0,656	yes	1,02	35	0,903	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		-0,247	yes	6,38	30	6,144	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 4																
Min.oil-GC	mg/l	V1		-2,409	yes	1,02	35	0,59	1,035	1,018	0,2242	22,0	16	1	0	17
Laboratory 5																
Min.oil-GC	mg/ml	S1		-0,667	yes	12	20	11,2	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		-1,059	yes	1,02	35	0,831	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		-1,452	yes	6,38	30	4,99	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 6																
Min.oil-GC	mg/ml	S1		3,750	yes	12	20	16,5	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		0,952	yes	1,02	35	1,19	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		0,345	yes	6,38	30	6,71	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 7																
Min.oil-GC	mg/ml	S1		-1,917	yes	12	20	9,70	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		6,667	H	1,02	35	2,21	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		1,254	yes	6,38	30	7,58	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 8																
Min.oil-GC	mg/ml	S1		0,333	yes	12	20	12,4	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		-1,457	yes	1,02	35	0,76	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		-2,027	yes	6,38	30	4,44	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 9																
Min.oil-GC	mg/ml	S1		-0,417	yes	12	20	11,5	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		-0,213	yes	1,02	35	0,982	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		0,366	yes	6,38	30	6,73	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 10																
Min.oil-GC	mg/ml	S1		-1,083	yes	12	20	10,7	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		-1,513	yes	1,02	35	0,75	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		-1,672	yes	6,38	30	4,78	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 11																
Min.oil-GC	mg/ml	S1		1,075	yes	12	20	13,29	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		0,448	yes	1,02	35	1,10	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		0,282	yes	6,38	30	6,65	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 12																
Min.oil-GC	mg/ml	S1		0,250	yes	12	20	12,3	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		-0,448	yes	1,02	35	0,94	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		0,209	yes	6,38	30	6,58	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 13																
Min.oil-GC	mg/ml	S1		-5,417	H	12	20	5,5	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V2		-1,964	yes	6,38	30	4,5	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 14																
Min.oil-GC	mg/l	V1		2,521	yes	1,02	35	1,47	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		-1,014	yes	6,38	30	5,41	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 15																
Min.oil-GC	mg/ml	S1		-0,183	yes	12	20	11,78	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		0,952	yes	1,02	35	1,19	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		1,390	yes	6,38	30	7,71	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 16																
Min.oil-GC	mg/ml	S1		1,750	yes	12	20	14,1	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		0,616	yes	1,02	35	1,13	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		0,481	yes	6,38	30	6,84	6,71	6,393	1,157	18,1	17	0	0	17

Outlier test failed. C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl fai-led	Mis-sing	Num of labs
Laboratory 17																
Min.oil-GC	mg/ml	S1		-0,250	yes	12	20	11,7	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		0,224	yes	1,02	35	1,06	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		0,439	yes	6,38	30	6,80	6,71	6,393	1,157	18,1	17	0	0	17
Laboratory 18																
Min.oil-GC	mg/ml	S1		0,058	yes	12	20	12,07	12,07	12,22	1,625	13,2	15	1	0	16
	mg/l	V1		1,681	yes	1,02	35	1,32	1,035	1,018	0,2242	22,0	16	1	0	17
	mg/l	V2		1,599	yes	6,38	30	7,91	6,71	6,393	1,157	18,1	17	0	0	17

Outlier test failed C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

ANNEX 9. SUMMARY OF THE z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	%
Min.oil-GC	S1	A	A	A		A	P	A	A	A	A	A	A	N		A	A	A	A	88
	V1	A	A	A	n	A	A	P	A	A	A	A	A	.	p	A	A	A	A	82
	V2	A	A	A	.	A	A	A	n	A	A	A	A	A	A	A	A	A	A	94
%		100	100	100	0	100	67	67	67	100	100	100	100	50	50	100	100	100	100	
Accredited		yes	yes	yes						yes	yes					yes				

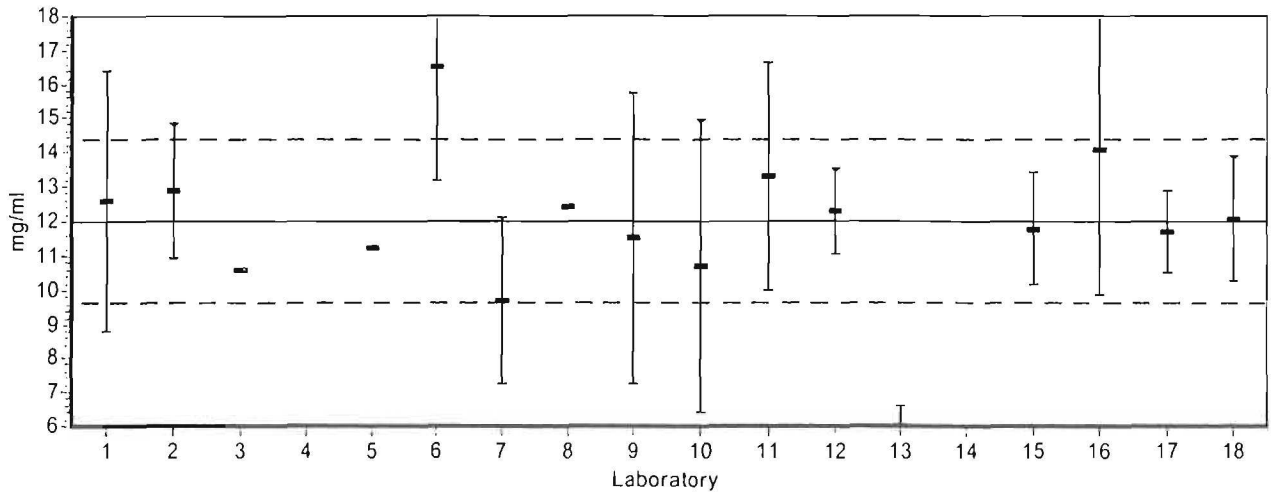
A - accepted ($-2 \leq Z \leq 2$), p - questionable ($2 < Z \leq 3$), n - questionable ($-3 \leq Z < -2$), P - non-accepted ($Z > 3$), N - non-accepted ($Z < -3$),

%* - percentage of accepted results

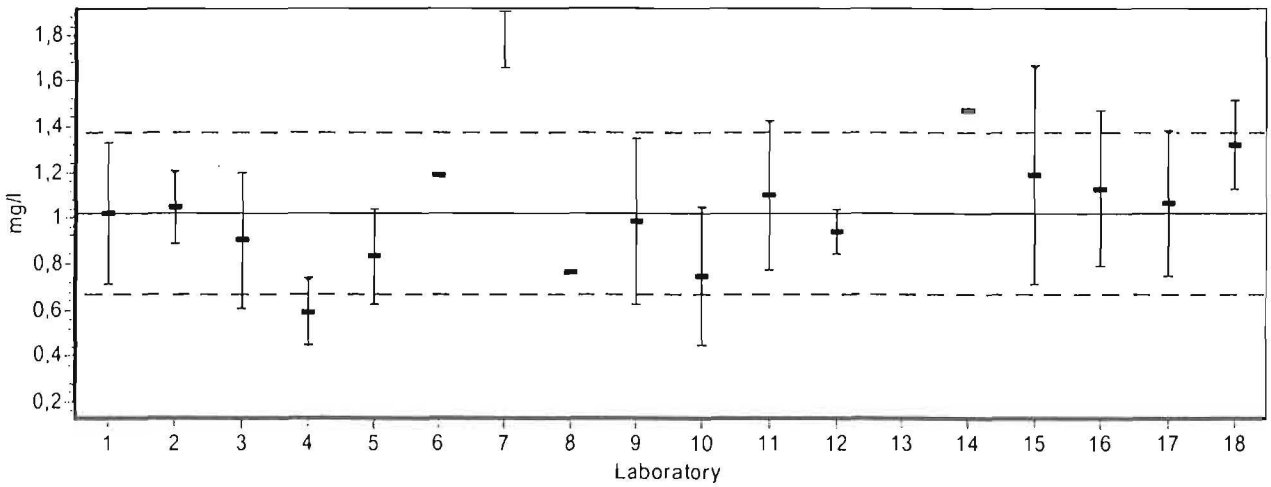
Totally accepted, % In all: 88 In accredited: 100

ANNEX 10. RESULTS AND MEASUREMENT UNCERTAINTIES REPORTED BY THE PARTICIPANTS

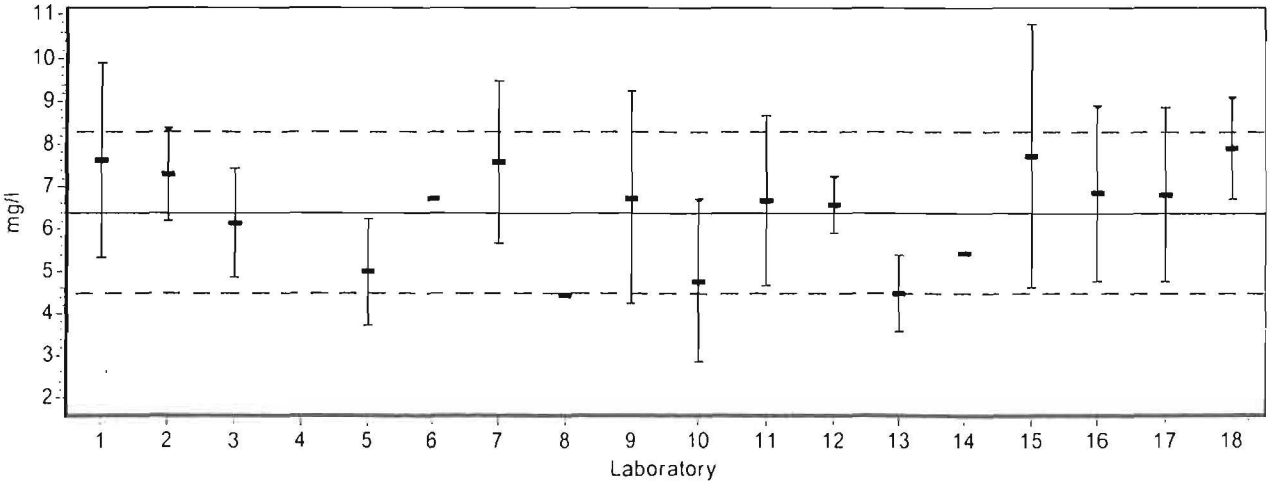
Analyytti *(Analyte)* **Min.oil-GC** Näyte *(Sample)* S1



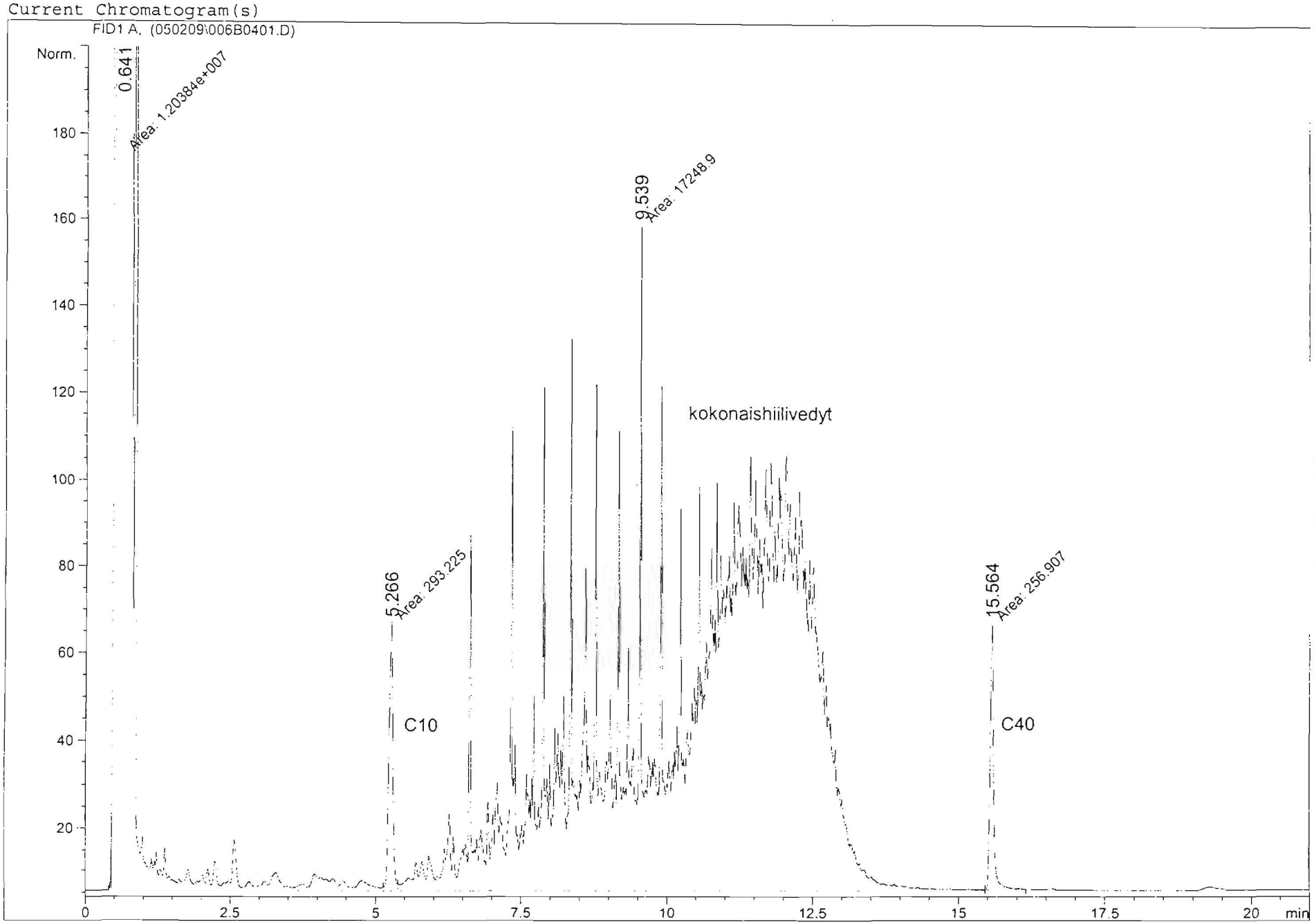
Analyytti *(Analyte)* **Min.oil-GC** Näyte *(Sample)* V1



Analyytti *(Analyte)* **Min.oil-GC** Näyte *(Sample)* V2

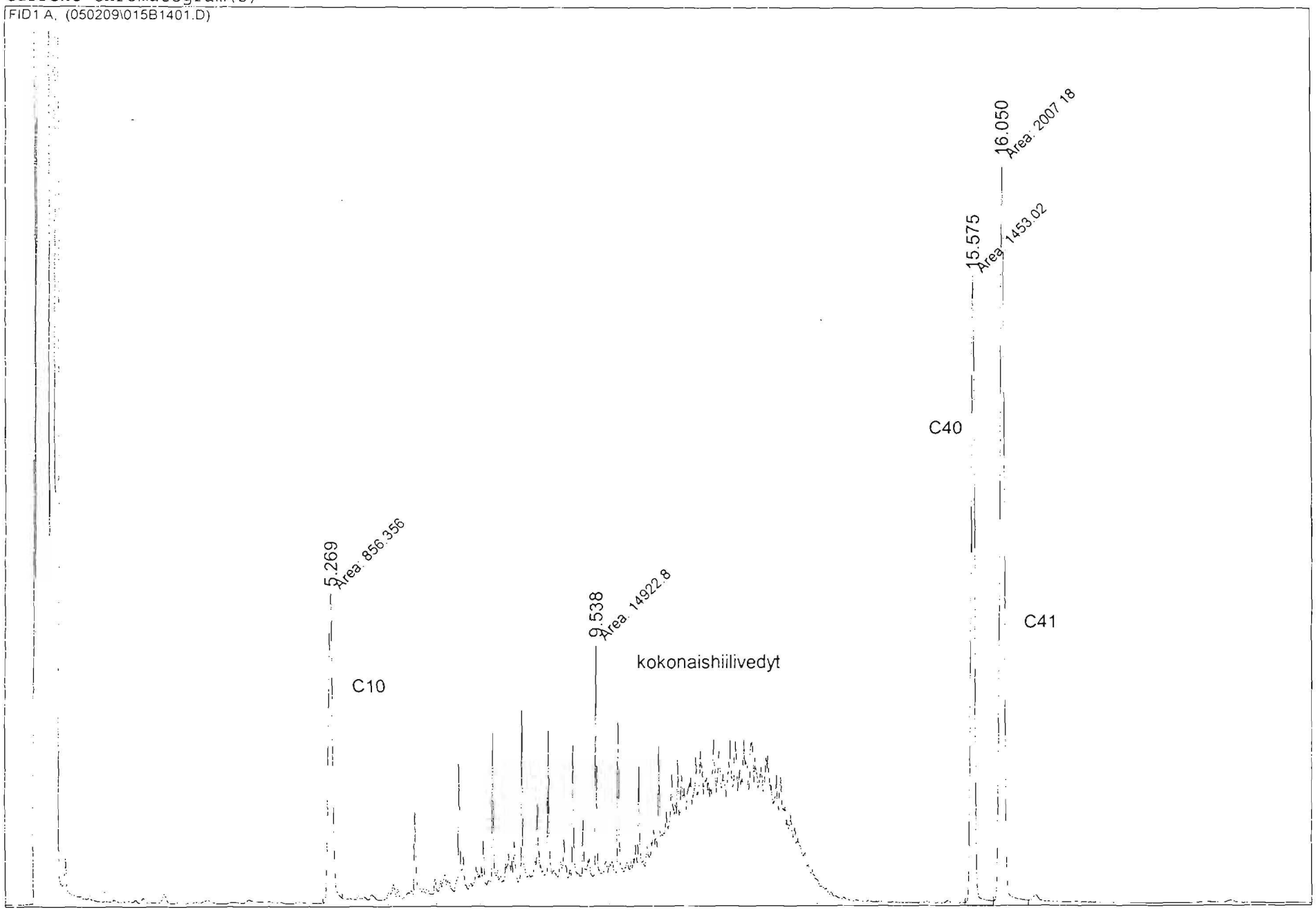


ANNEX 11. EXAMPLE OF SAMPLE CHROMATOGRAM



Current Chromatogram(s)

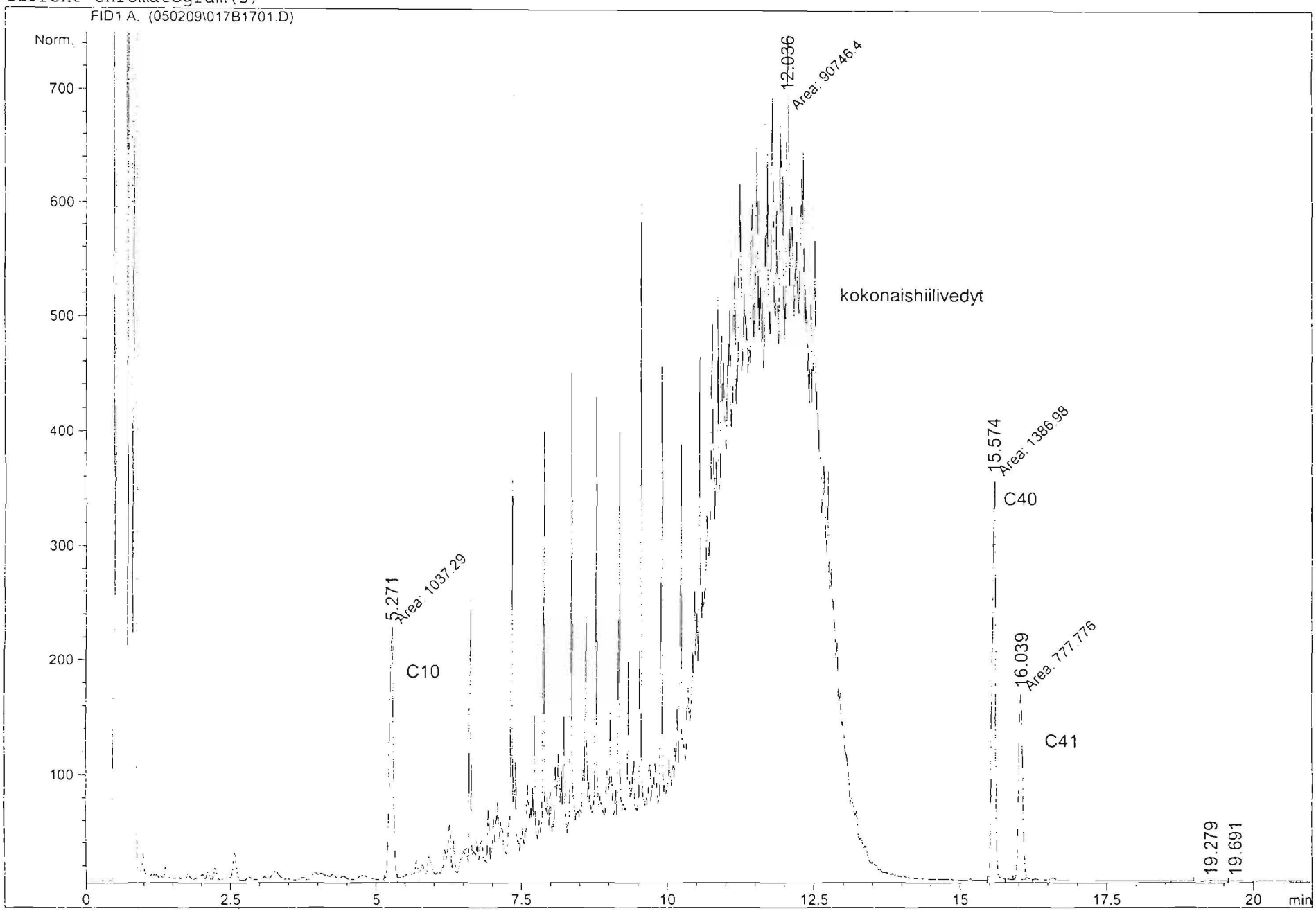
FID1 A, (050209\015B1401.D)



ANNEX 11/2

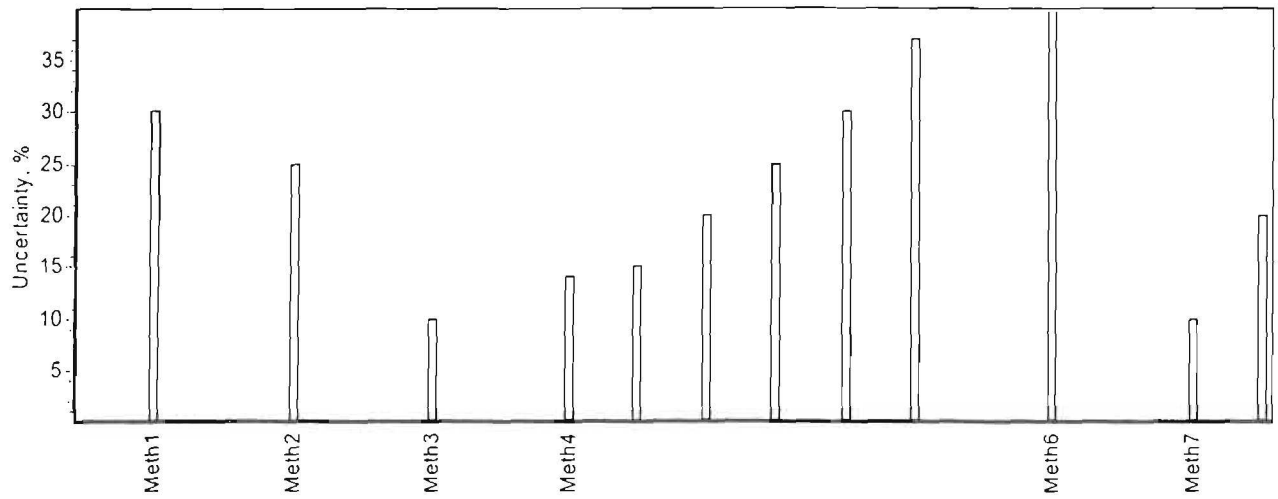
strument 1 6/21/2005 10:43:05 AM MS

Current Chromatogram(s)

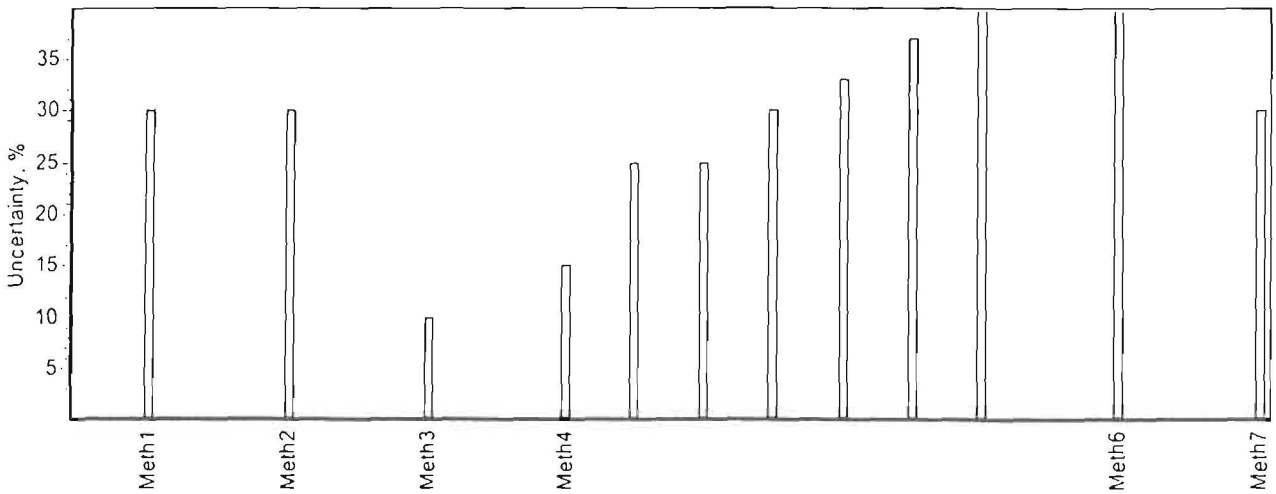


ANNEX 12. MEASUREMENT UNCERTAINTIES ESTIMATED BY USING DIFFERENT PROCEDURES

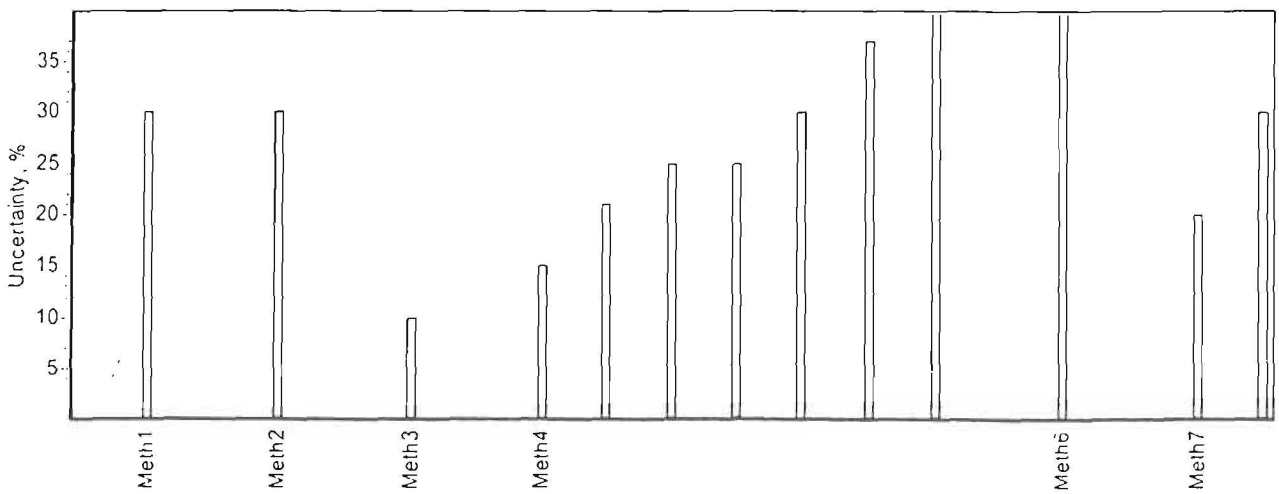
Analyytti *(Analyte)* **Min.oil-GC** Näyte *(Sample)* S1



Analyytti *(Analyte)* **Min.oil-GC** Näyte *(Sample)* V1



Analyytti *(Analyte)* **Min.oil-GC** Näyte *(Sample)* V2



Measurement uncertainties were estimated by using the procedures as follows:

1. the variation of the results in X chart (for artificial samples)
2. the variation of the results in X chart and the variation of the replicates (r- or R- chart for real samples)
3. the variation of the data obtained in analysis of CRM
4. the data obtained in method validation (and IQC)
5. the EURACHEM-Guide "Quantifying Uncertainty in Analytical Measurements"
6. the NORDTEST report TR 537
7. other procedure

Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date Juni 2005
Author(s)	Irma Mäkinen and Pirjo Sainio	
Title of publication	SYKE Proficiency test 8/2004 (mineral oil hydrocarbons in water)	
Parts of publication/ other project publications		
Abstract	The Finnish Environment Institute carried out the profiency test for analysis of mineral oil hydrocarbons in waters by using GC methods in February 2005. A total of 18 laboratories from Finland and Sweden participated. One standard solution containing a known concentration of different oils was prepared. Two solutions containing different oils were prepared to be used as the addition solutions for the preparation of water samples. One river water sample and one lake water sample were delivered. For the synthetic sample the calculated mineral oil content was used as the assigned value. For the analysis of the water samples the robust mean value was used as the assigned value. In this proficiency test, 88 % of the participating laboratories reported satisfactory results based on the target total standard deviation 20% – 35% used in calculating of z scores in 95 % confidence interval. Six participants used the accredited analytical methods and 100% from their results were satisfactory. The Finnish proficiency test for analysis of mineral oil hydrocarbons in waters by using the GC method was carried out for the second time. These results have improved since the last comparison in 2002.	
Keywords	water analysis, mineral oil, hydrocarbons, environmental laboratories, proficiency test, interlaboratory comparisons	
Publication series and number	Suomen ympäristökeskuksen moniste 326	
Theme of publication		
Project name and number, if any		
Financier/ commissioner		
Project organization		
	ISSN 1455-0792	ISBN 952-11-2020-7
	No. of pages 31	Language English
	Restrictions Public	Price
For sale at/ distributor	Finnish Environment Institute, Customer service E-mail: neuvonta.syke@ymparisto.fi tel. 358 9 4030 0190, fax 358 9 40300 190	
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Printing place and year	Edita Prima Ltd, Helsinki 2005	
Other information		

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Kesäkuu 2005
Tekijä(t)	Irma Mäkinen ja Pirjo Sainio	
Julkaisun nimi	SYKE Proficiency Test 8/2004 (mineral oil hydrocarbons in water) SYKE pätevyyskoe 8/2004 (mineraaliöljyt vedestä)	
Julkaisun osat/ muut saman projektin tuottamat julkaisut		
Tiivistelmä	Suomen ympäristökeskus järjesti helmikuussa 2005 pätevyyskokeen mineraaliöljyn määrittämiseksi vedestä. Pätevyyskokeessa käytettiin yhtä poikkeusta lukuun ottamatta kaasukromatografisia määritysmenetelmiä. Pätevyyskokeeseen osallistui kaikkiaan 18 laboratoriota Suomesta ja Ruotsista. Pätevyyskokeen näytteinä oli yksi tunnetun öljypitoisuuden omaava standardiliuos ja kaksi vesinäytettä, joihin osallistuva laboratorio teki toimitetut mineraaliöljylisäykset. Synteettiselle näytteelle käytettiin vertailuarvona laskennallista öljypitoisuutta. Vesinäytteille vertailuarvona käytettiin robusti-keskiarvoa. Tässä pätevyyskokeessa osallistujien tuloksista 88% oli tyydyttäviä, kun z-arvojen laskennassa käytettiin 20% – 35 %:n tavoitekokonaiskeskihajontoja (95 % merkitsevyystasolla). Vesinäytteiden analysoinnissa esiintyi joitakin eroja analyysimenetelmän eri vaiheissa (mm. uutto, puhdistus), joilla on ollut vaikutusta tuloksiin. Määritysmenetelmänsä akkreditoineiden laboratorioiden tuloksista 100% oli tyydyttäviä. Pätevyyskoe mineraaliöljyn määrittämiseksi vesistä GC-menetelmää käyttäville laboratorioille järjestettiin toisen kerran Suomessa. Tulokset olivat parantuneet edellisestä pätevyyskokeesta, joka järjestettiin vuonna 2002.	
Asiasanat	vesinäytteet, mineraaliöljyt, hiilivedyt, ympäristölaboratoriot, pätevyyskoe, vertailukoe	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen moniste 326	
Julkaisun teema		
Projektihankkeen nimi ja projektinumero		
Rahoittaja/ toimeksiantaja		
Projektiryhmään kuuluvat organisaatiot		
	ISSN 1455-0792	ISBN 952-11-2020-7
	Sivuja 31	Kieli englanti
	Luottamuksellisuus Julkinen	Hinta
Julkaisun myynti/ jakaja	Suomen ympäristökeskus, asiakaspalvelu sähköpostiosoite: neuvonta.syke@ymparisto.fi puh. (09) 4030 0119, telefax (09) 4030 0190	
Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2005	
Muut tiedot		

Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum Juni 2005
Författare	Irma Mäkinen och Pirjo Sainio	
Publikationens titel	SYKE Provningsjämförelse 8/2004 (mineralolja i vatten)	
Publikationens delar/ andra publikationer inom samma projekt		
Sammandrag	Under Mars 2004 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämningen av mineralolja med GC i ett syntetiskt prov och i två vattenprov (ett sjövatten och ett flodvatten). Laboratorierna tillsatte de sända mineralolja blandningarna till vattenproven. Proven sändes ut till 18 laboratorier i Finland och i Sverige. Laboratorierna använde en GC analysmetod förutom ett laboratorium, som använde gravimetriska metoden. Skillnaderna i metoderna använda av deltagarna hade haft någon inverkan på resultaten. Resultaten värderades med hjälp av z-värden. Beräkningen av z-värdena baserade sig på totalstandardavvikelser, som sattes till 20 % eller 35 % (95 % sannolikhetsnivå). Det teoretiska värdet eller robust-medelvärdet användes som referensvärde (*the assigned value*). I provningsjämförelsen var 88 % av resultaten nöjaktiga. Sex laboratorier använde ackrediterade analysmetoder och 100 % av deras resultat var nöjaktiga. Jämförelsen genomfördes för andra gången för GC-metoden. Resultaten förbättrades från den förra jämförelsen 2002.	
Nyckelord	vattenanalyser, mineral olja, hydrocarbons, provningsjämförelse, miljölaboratorier	
Publikationsserie och nummer	Suomen ympäristökeskuksen moniste 326	
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Övriga uppgifter		

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